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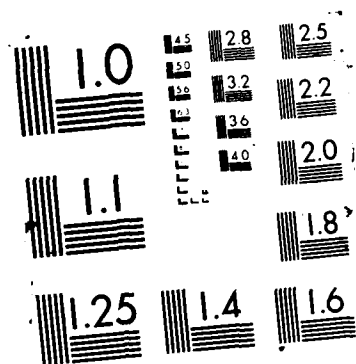
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LASER ACTION FROM SYN-(METHYL,METHYL) BIMANE

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ABSTRACT

Under the flashlamp excitation from an aqueous solution of syn-(methyl, methyl)bimane laser action was observed at 504 nm. The absorption, fluorescence, and triplet-triplet absorption spectra of this compound was also recorded. This compound showed good photochemical stability. The laser action properties of this new laser dye were compared with those of Coumarin 30.

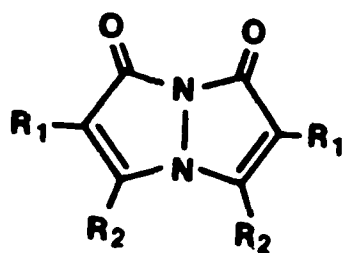
INTRODUCTION

At present, the coumarin laser dyes are the ones most widely used for the spectral region stretching from 440 to 550 nm. However, the coumarin dyes have rather poor photochemical stability.

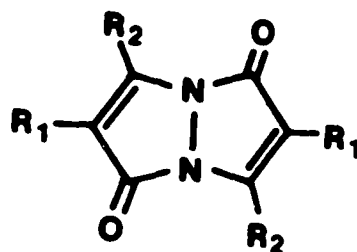
While searching for more stable and efficient laser dyes, we studied 3,4,6,7-tetramethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione [syn-(CH₃)₄B for short]. This new heterocyclic molecule was first reported by Kosower et al. in 1978 [1]. Their work included the observation of the strong and striking fluorescence properties, as well as good photochemical stability of these compounds. It should be emphasized that strong fluorescence (high quantum fluorescence yield) of organic compounds which are not benzene derivatives is rare. The quantum fluorescence yield of the syn-(R₂,R₁)B ranges from 0.7 to 0.9 [1]. The isomer anti-(R₂,R₁)B is only weakly fluorescent.

There are two specific spectroscopic parameters of laser dyes which critically determine the laser action efficiency of flashlamp and cw laser pumped dye lasers: (a) A high quantum fluorescence yield, and (b) Low triplet-triplet (T-T) absorption over the fluorescence (laser action) spectral region of the laser dye.

We, therefore, recorded the T-T absorption spectrum of syn-(CH₃.CH₃)B. We compared the laser action parameters of syn-(CH₃.CH₃)B with those of coumarin 30. Both. syn-(CH₃.CH₃)B and coumarin 30 showed laser action in the same spectral region. Syn-(CH₃.CH₃)B lased only 30 percent less efficient than did coumarin 30.



syn-(R₂,R₁)bimane



anti-(R₂,R₁)bimane

EXPERIMENTAL

Spectroscopic Equipment

We used the same equipment described by Pavlopoulos [2] to measure the absorption (S-S), fluorescence, and T-T absorption of syn-(CH₃.CH₃)B. As excitation source for recording the T-T absorption spectrum, we used the 351/356 nm lines of a Spectra-Physics krypton ion cw laser.

Dye Laser

A small EGG #FX139C-2 flashlamp pumped dye laser was used for the experiments. The flashlamp produced pulses of approximately 200 η sec risetime and 600 η sec length at the halfwidth of the pulse. It delivered two Joules at 6.32 kVolt, five Joules at 10.0 kVolt, and ten Joules at 14.14 kVolt. The dye laser was used in the nonflowing (static) mode. The dye cell was about 2.5 mm diameter and 50 mm long, positioned in a single ellipsoidal cavity of small eccentricity. The intensity of the laser pulses, which were measured with a photomultiplier, were reduced by several Jenaer Glaswerk neutral density filters and displayed on the screen of a Tektronix 7834 storage oscilloscope.

RESULTS AND DISCUSSION

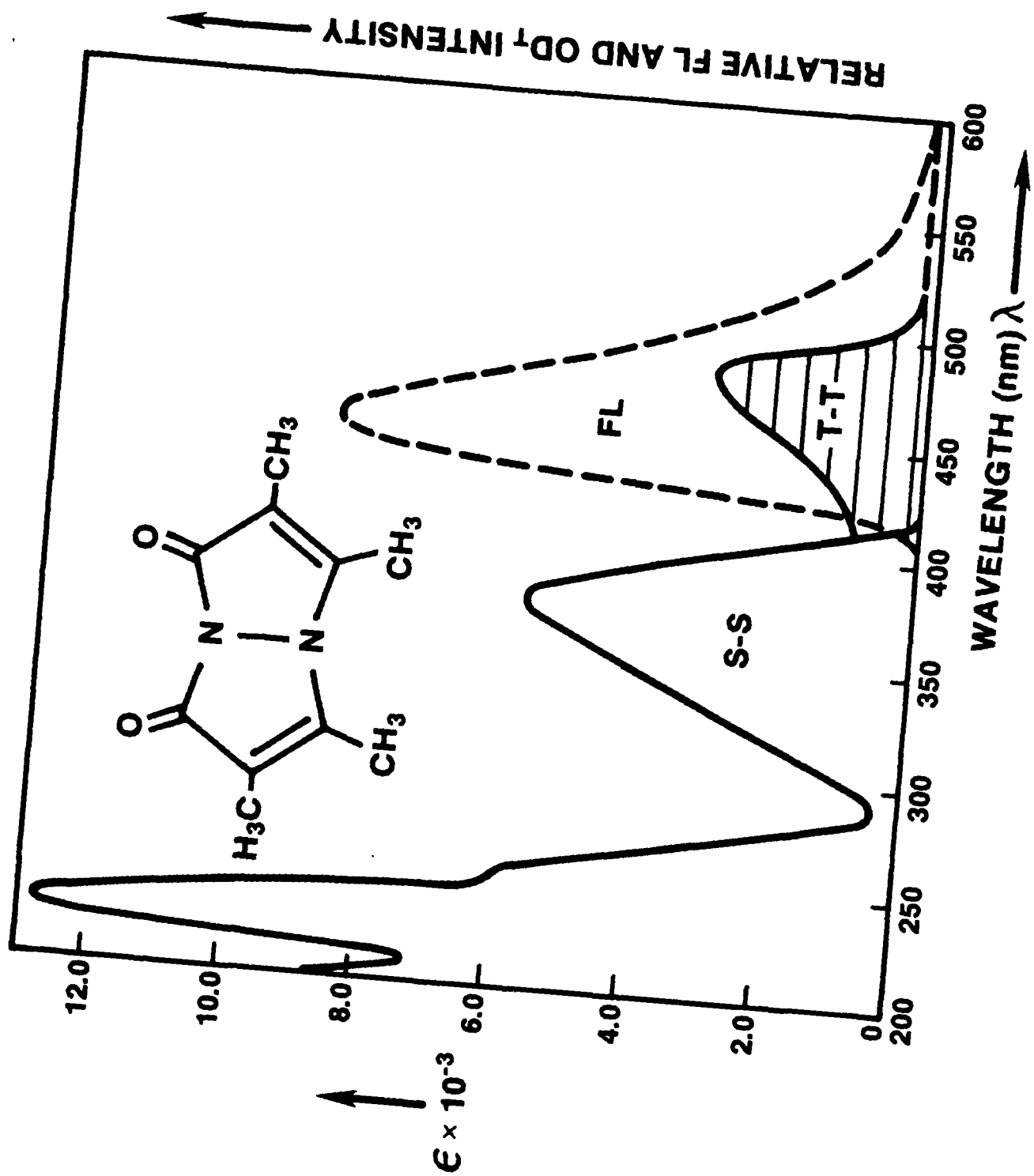
Electronic Spectra

Another unusual property of the syn-bimanes is their remarkable dependence on the spectral location of their lowest energy absorption band (S-S) on the solvent employed. Consequently, the spectral location of the fluorescence is also very much solvent dependent [1.3]. For example, the fluorescence maximum for syn-(CH₃.CH₃)B, the compound we studied, shifts from 420 nm in p-dioxan to 460 nm in ethanol to 480 nm in water. However, we found laser action under flashlamp excitation from this compound only in water and hexafluoroisopropanol solutions.

The T-T absorption spectra of organic compounds are measured at liquid nitrogen temperatures to extend the lifetime of the triplet state molecules. For this measurement, the organic compound must be dissolved in a solvent which freezes in clear, glasslike solid at liquid nitrogen temperature. We dissolved the syn-(CH₃CH₃)B in the following solvents: ethanol/ethyl ether 2:1 ratio, 2-methyltetrahydrofuran, EPA, and n-butanol/isopentane in 3:7 ratio.

Syn-(CH₃,CH₃)B showed a fluorescence intensity maximum in the blue region (450 to 460 nm) of the spectrum in all of these glassy solvents we tried. We did not find any glassy solvents in which syn-(CH₃,CH₃)B would give blue/green (480 nm) fluorescence as in water and hexafluoroisopropanol.

Figure 1 shows the absorption (S-S), the T-T absorption, and the fluorescence spectrum of syn-(CH₃,CH₃)B dissolved in 2:1 ratio ethanol/ethyl ether. It is apparent that some T-T absorption overlaps the fluorescence spectral region. This compound has a T-T absorption band located in the fluorescence region with its maximum at 490 nm. The intensity of this T-T absorption bands drops rather rapidly toward the long wavelengths. This would then explain why this compound showed laser action in the green spectral region, and not in the blue spectral region.



The photo stability under krypton ion cw laser excitation at 351/356 nm of syn-(CH₃,CH₃)B was remarkably good in the different glassy solvents we employed. This exceptional stability under irradiation with 360 nm light was already observed by Kosower et al. [3]. This is in contrast to the coumarin laser dyes where photodecomposition reduces measurement accuracy when recording the T-T absorption spectra [2].

Laser Experiments

We observed laser action from syn-(CH₃,CH₃)B broadband at 504 nm, with a threshold at 9.6 kVolt, using a 5×10^{-4} molar solution in distilled water. A 2×10^{-4} molar solution had its threshold at 13.4 kVolt. We did not observe any laser action in a 1×10^{-4} molar solution pumping with 14.5 kVolt.

By comparison, a 2×10^{-4} molar solution of coumarin 30 in ethanol did exhibit laser action at 506 nm with threshold at 6.7 kVolt.

The pulses were displayed on the storage oscilloscope and photographed. By measuring the area (integration) of the intensity-time curve, the relative intensity of the laser pulses were obtained. From these measurements it was concluded that syn-(CH₃,CH₃)B lases with about 1/3 less efficiency than does coumarin 30. Both dyes were pumped at 12 kVolt. In solvents conventionally used to dissolve laser dyes, such as p-dioxan, ethanol, dimethyl formamide, we did not observe any laser action when pumped up to 14.5 kVolts. In all these solvents, the fluorescence maximum

located in the 420 to 460 nm spectral region. However, we observed laser action of syn-(CH₃,CH₃)B in a 1×10^{-3} molar solution of hexafluoroisopropanol, where syn-(CH₃,CH₃)B showed blue/green fluorescence, with intensity maximum at 480 nm. Laser emission occurred at 501 nm with threshold at 9.9 kV. In a 5×10^{-4} molar solution, however, pumping with up to 14.5 kV failed to produce laser action.

Discussion

The reason that syn-(CH₃,CH₃)B shows laser action only in water and in hexafluoroisopropanol, and only at higher concentrations is somewhat difficult to explain. We mentioned the solvent dependency of the spectral location of the lowest energy S-S absorption band, and consequently of the spectral location of the fluorescence spectrum of syn-(CH₃,CH₃)B. Unfortunately, we do not know whether the spectral location of the lowest energy T-T absorption band, which is located at about 490 nm in the ethanol/ethyl ether solution, is solvent dependent or not. The fact that we do observe laser action in the two solvents, which causes the largest red shift of the fluorescence band (peak), suggests that the T-T absorption band located at 490 nm was probably not much red shifted. However, the observation that laser action takes place only at higher syn-(CH₃,CH₃)B concentrations may suggest that some sort of triplet/triplet annihilation mechanism is present. It is well known, from experiments on pure crystals of organic compounds, that no T-T absorption is observed due to triplet/triplet annihilation. Nevertheless, other explanations cannot be ruled out.

In conclusion, the bimanies appear to be a new class of potential laser dyes. By using different groups (e.g. auxochromic substituents) for R₁ and R₂ [4], one should be able to shift the T-T absorption band out of the fluorescence mission (laser action) region.

Higher efficiency resulting from the reduced T-T absorption, combined with the high quantum efficiency of the bimanes, their good solubility in many solvents (including water), and their good photochemical stability should make these new laser dyes very competitive to the presently available laser dyes.

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